

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) July 2014		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To) July 2014- August 2014	
4. TITLE AND SUBTITLE New approaches to maximizing thermo-oxidation resistance of polycyanurate networks				5a. CONTRACT NUMBER In-House	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Andrew J. Guenthner, Matthew C. Davis, Vandana Vij, Gregory R. Yandek, Kevin R. Lamison , Josiah T. Reams, Timothy S. Haddad, Joseph M. Mabry				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER Q0BG	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NO.	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive. Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-VG-2014-230	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited.					
13. SUPPLEMENTARY NOTES Briefing Charts presented at ACS Fall National Meeting, San Francisco, CA, 13 August 2014. PA#14390					
14. ABSTRACT Among thermosetting resins, polycyanurate networks (derived from cyanate ester monomers) offer excellent flame, smoke, and toxicity characteristics along with enhanced thermo-oxidative stability compared to epoxy resins. Recent structure-property investigations in polycyanurate networks have revealed new insights into the relationship between the chemical moieties found in the networks and the corresponding levels of thermo-oxidative resistance. In particular, it appears that the presence of methyl groups next to tertiary or quaternary carbons has a decidedly negative impact on thermo-oxidative stability during TGA heating ramp tests. In the case of silicon-containing cyanate esters, thermo-oxidative stability can be improved significantly by the incorporation of silicon only in cases where either a large portion of the chemical repeat unit is formed from inorganic groups, or the thermo-oxidative stability of the carbon-containing analog is relatively poor compared to other organic polycyanurate networks.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON Joseph Mabry
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) 661-275-6174



NEW APPROACHES TO MAXIMIZING THERMO-OXIDATION RESISTANCE OF POLYCYANURATE NETWORKS

13 August 2014

Andrew J. Guenthner¹, Matthew C. Davis², Vandana Vij³,
Gregory R. Yandek¹, Kevin R. Lamison³, Josiah T. Reams³,
Timothy S. Haddad³, Joseph M. Mabry¹

¹Aerospace Systems Directorate, Air Force Research Laboratory

²Naval Air Warfare Center, Weapons Division

³ERC Incorporated

Ph: 661/275-5769; e-mail: andrew.guenthner@us.af.mil

DISTRIBUTION A: Approved for public release; distribution is unlimited.



Outline



- Role of Bridge Type:
 - Avoid Ethylidene and Isopropylidene Bridges!
- Role of Si
 - High Inorganic Content Needed to Match the Gains from Proper Selection of Bridge Type
- Bio-based Materials
 - Resveratrol-based CE Delivers Exceptional Thermal Stability and Fire Resistance



Acknowledgements: Strategic Environmental Research and Development Program (SERDP); Air Force Office of Scientific Research (AFOSR)
– program support; PWG Team Members!





Cyanate Esters for Next-Generation Aerospace Systems



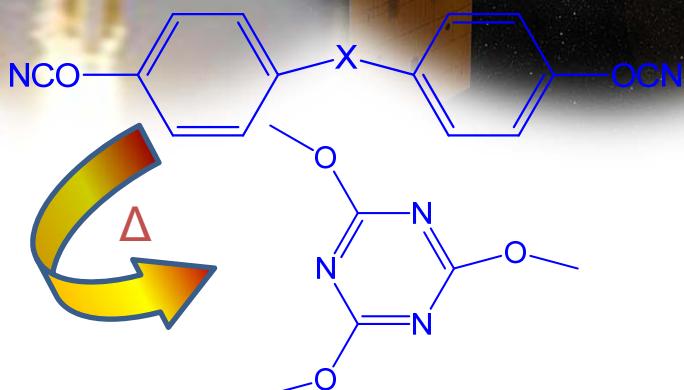
Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

Ease of Processing
Resistance to Harsh Environments



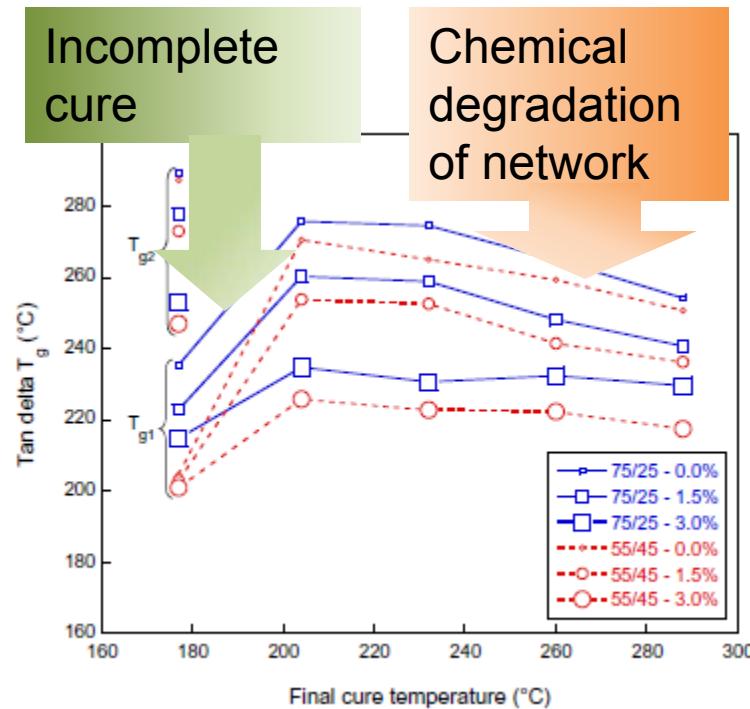
Onset of Weight Loss:
> 400 °C with High Char Yield

Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic Expansion



Thermo-mechanical versus Thermo-chemical Stability



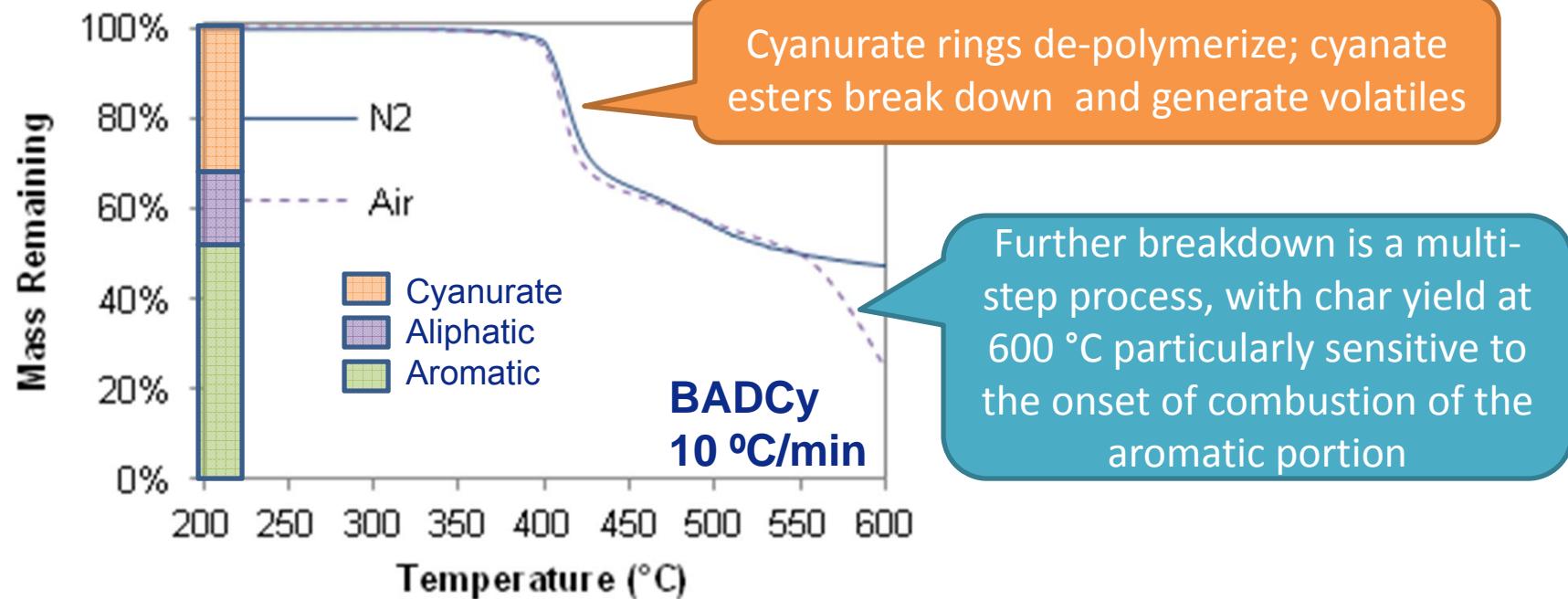
Goertzen, W. K.; Kessler, M. R. *Composites: Part A* 2007 38, 779–7, Fig. 6, for blends of EX1551 / EX1510 – catalyst.

- The more rigid the network, the higher the thermo-mechanical stability (i.e. softening point for a given network structure).
- Many networks cannot achieve their maximum possible thermo-mechanical stability because at the high temperatures needed for cure, chemical bonds break (i.e. thermochemical stability is limited).
- Typically, adding flexible chemical linkages (such as aliphatic groups) to the chemical structure of a monomer will reduce the rigidity, facilitating the achievement of full cure, but at the expense of thermo-chemical stability.

Needed: a flexible chemical linkage that enables full cure of cyanate esters at acceptable temperature-catalyst combinations while maintaining the desirable chemical degradation characteristics (both rates and char yields) of rigid systems



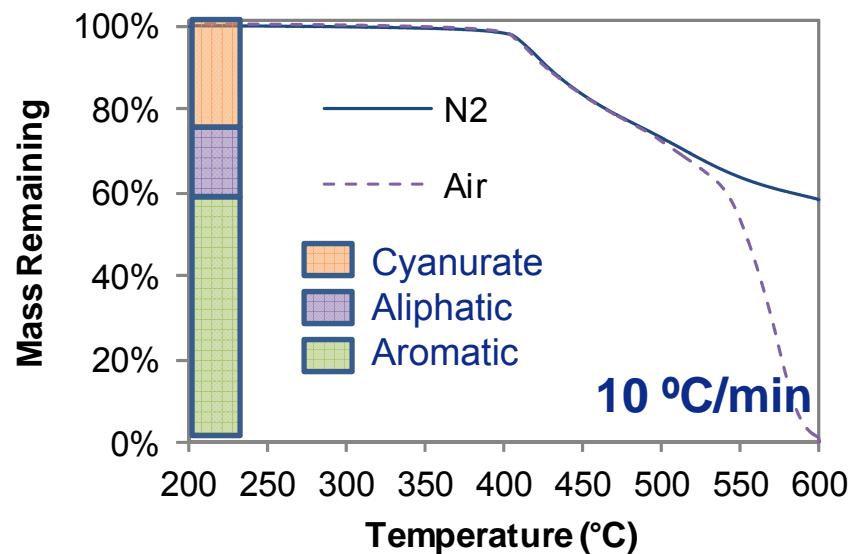
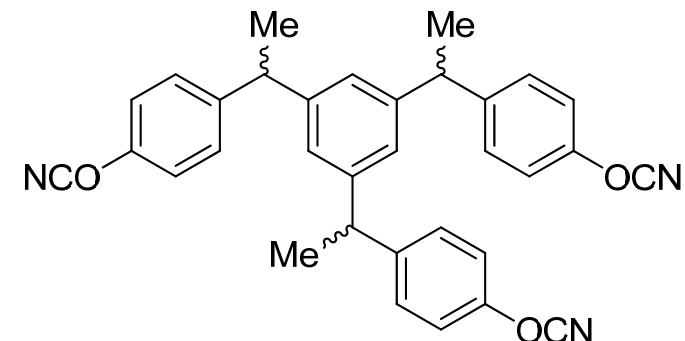
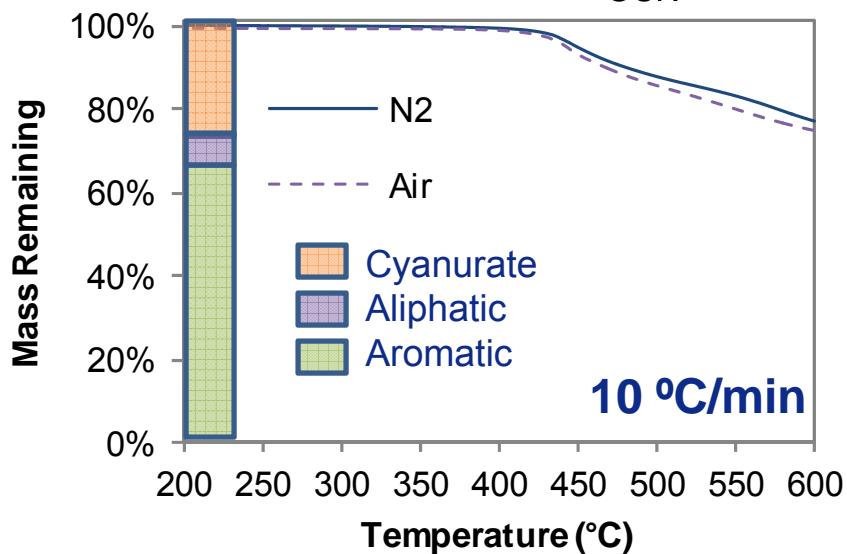
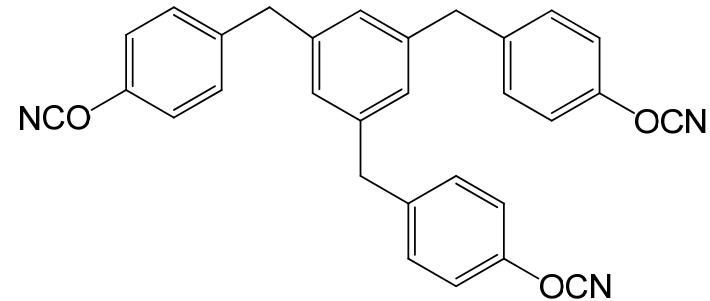
TGA of Cyanate Esters



- TGA provides a simple tool to assess onset temperatures, rates, and char yields associated with the decomposition of cyanate ester networks.
- A reasonably slow TGA scan also drives all cyanate ester systems close to the maximum possible extent of conversion (via *in-situ* cure) at the point where decomposition begins.



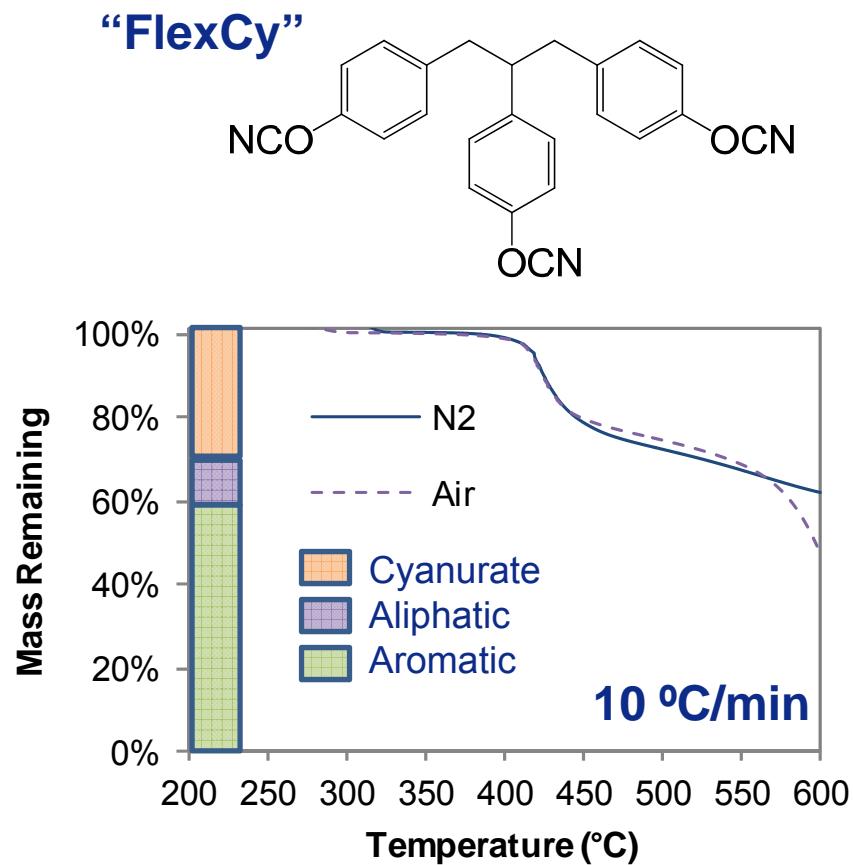
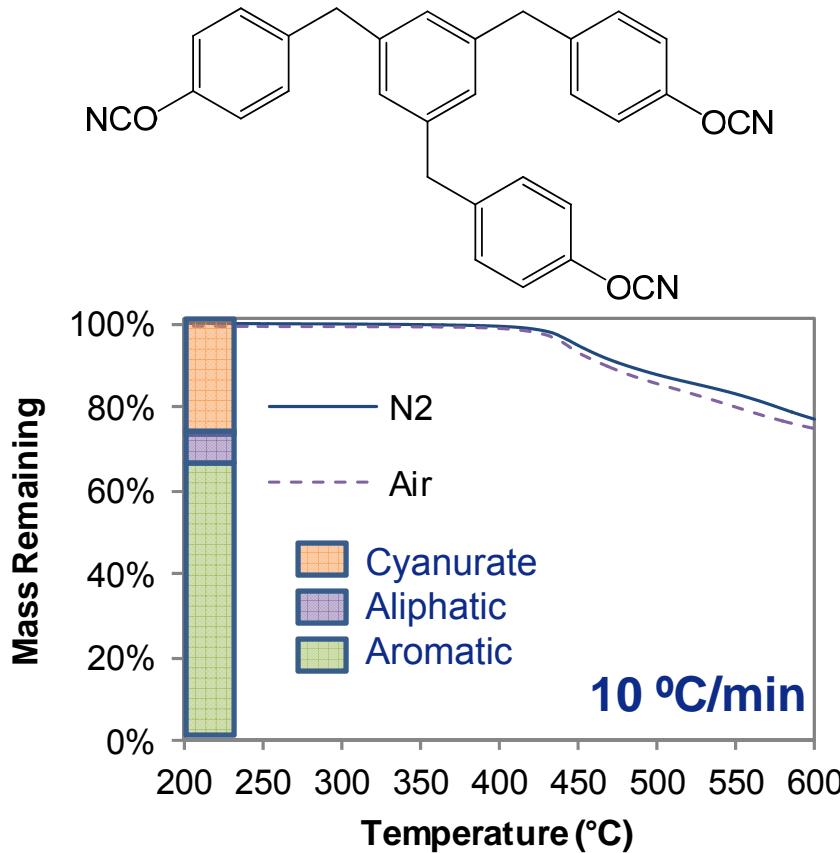
Cyanate Ester TGA: Methylene versus Ethylidene Segments



- The tricyanate with methylene segments shows delayed onset of degradation, reduced decomposition rates, and very high char yield.
- The tricyanate with ethylidene segments behaves much like BADCy when taking into account the composition, with slightly earlier aromatic combustion.



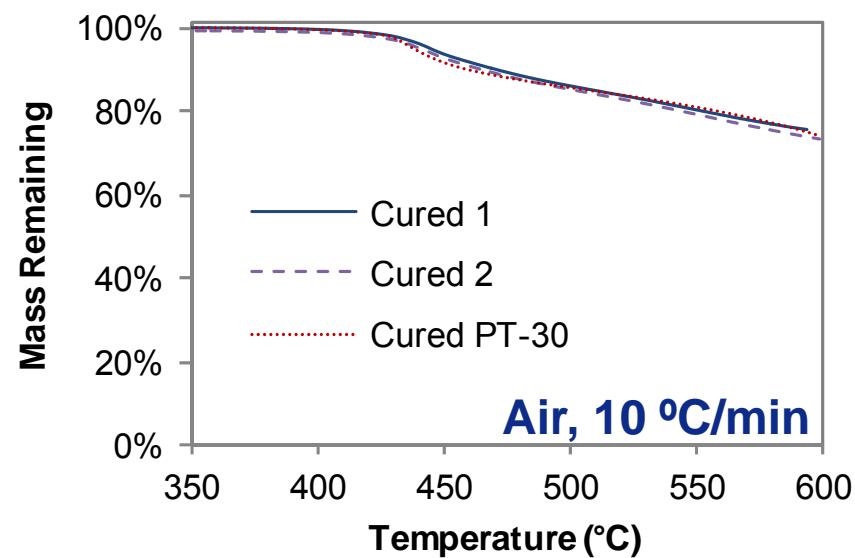
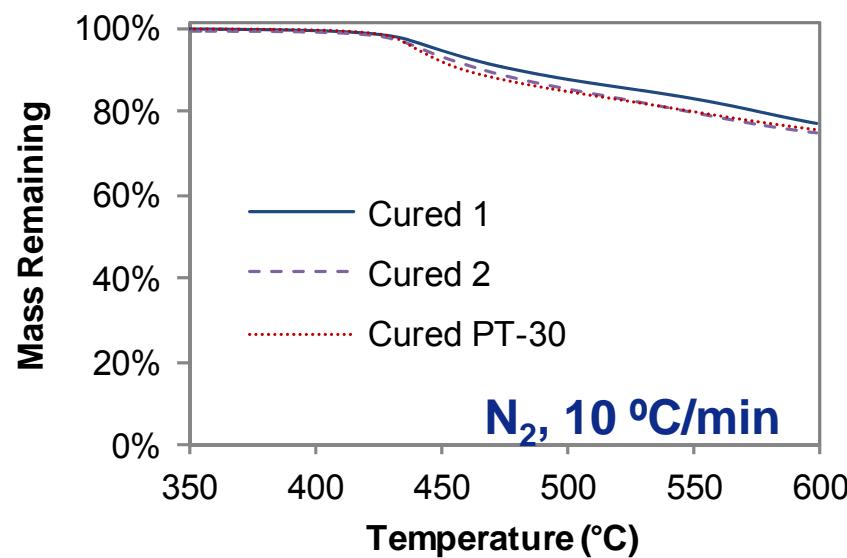
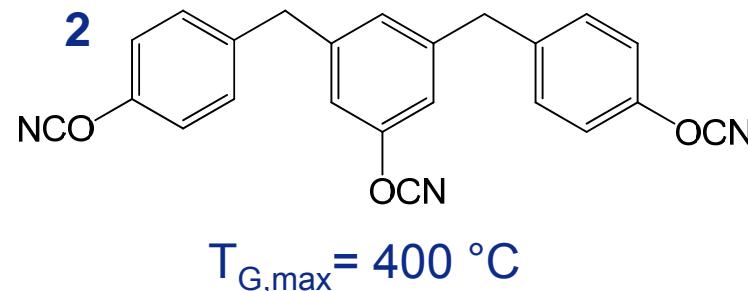
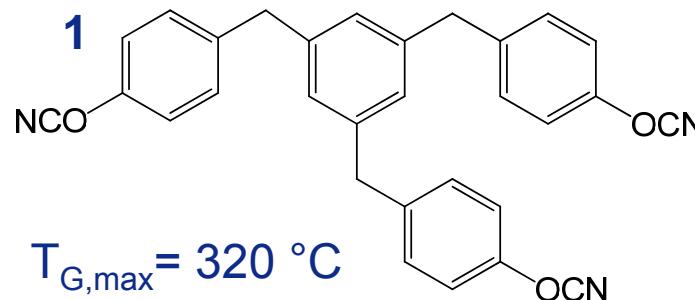
Cyanate Ester TGA: Aliphatic *versus* Aromatic Junctions



- The tricyanate with the aliphatic junction (tertiary carbon) also follows the pattern for BADCy, taking into account composition, with a slightly delayed onset of aromatic combustion compared to BADCy.



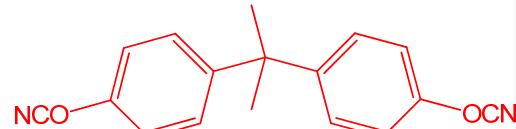
Segment Flexibility Can Be Tuned Without Affecting Char Yields



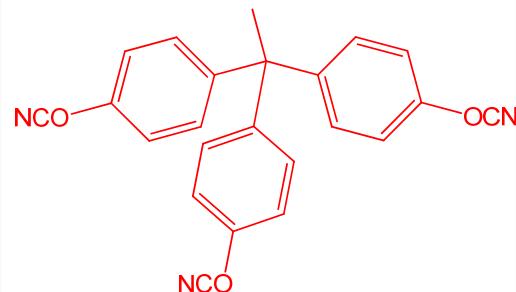
- Note that PT-30 is similar to an oligomeric version of 2.
- Tuneability of $T_{G,\max}$ enables full cure to be achieved with a wider range of catalysts under typical processing constraints.



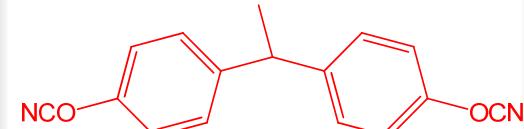
Si-Containing Cyanate Ester Monomers



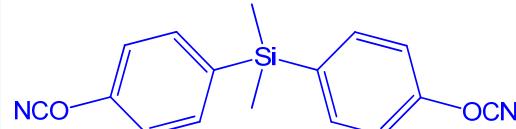
BADCy



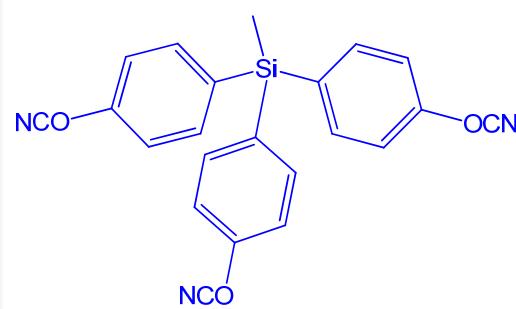
ESR255



LECy



SiMCy



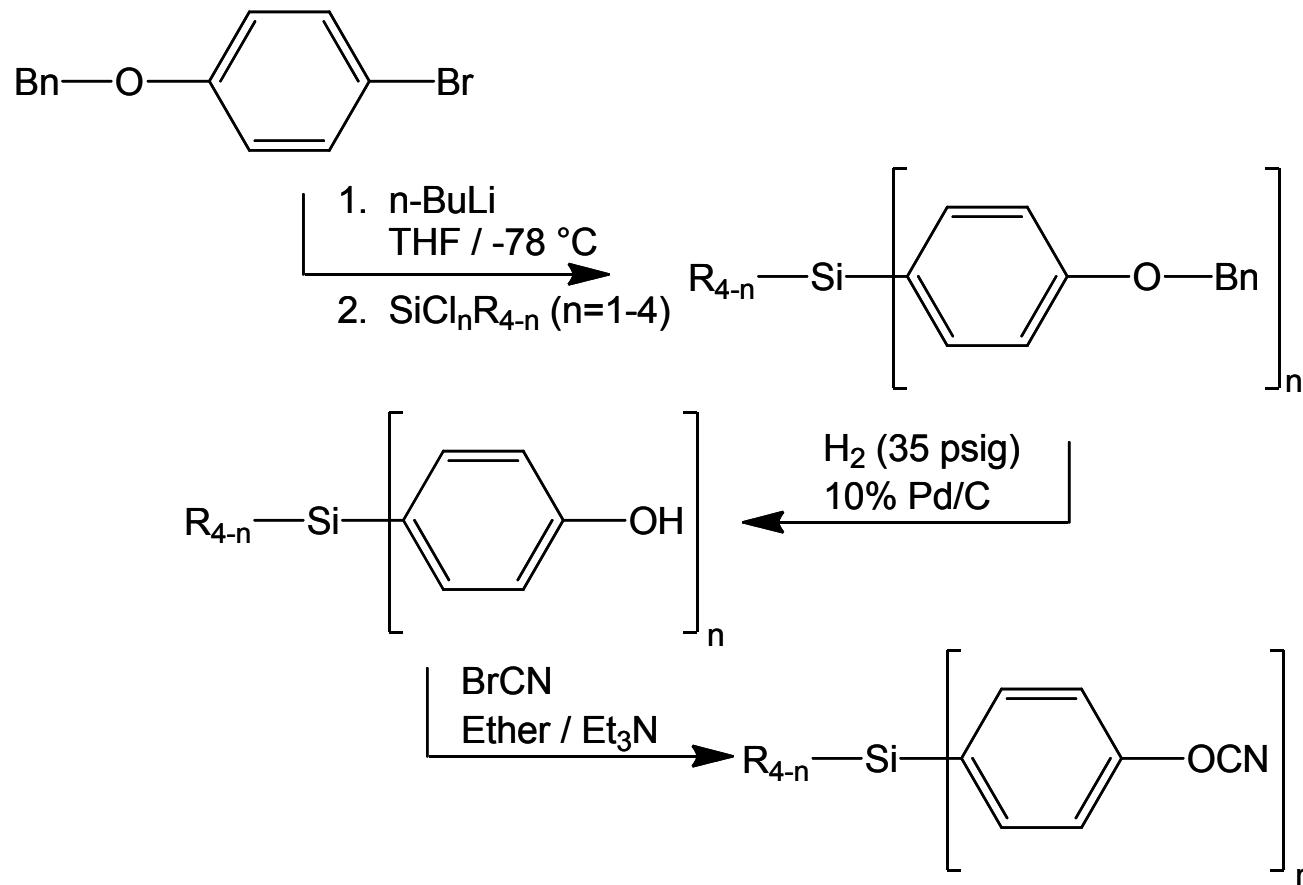
STT3

Catalyzed systems use:
160 ppm Cu(II) as Cu(II)(acac)₂
with 2 phr nonylphenol

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N₂, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.



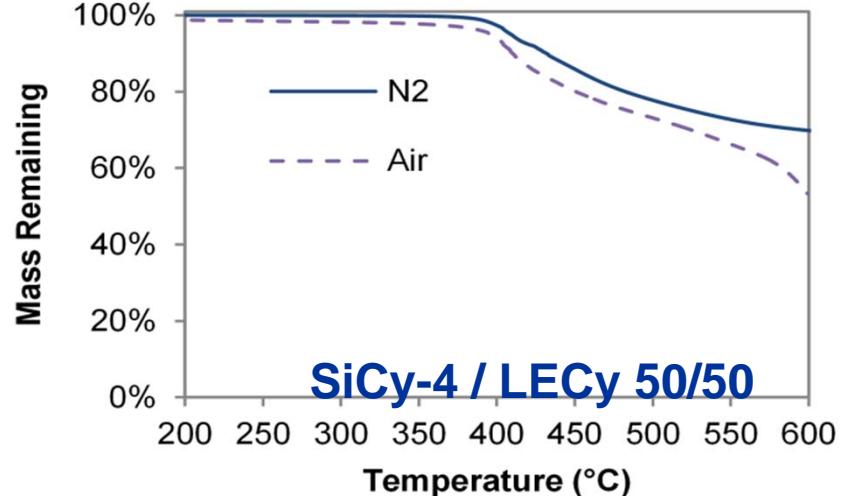
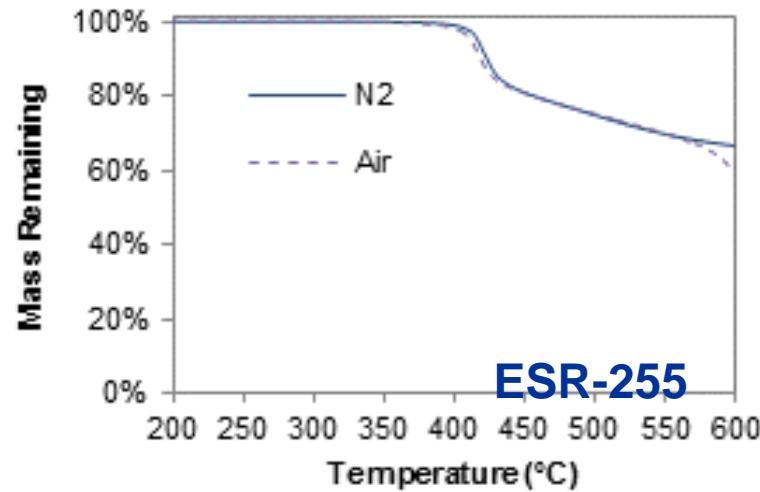
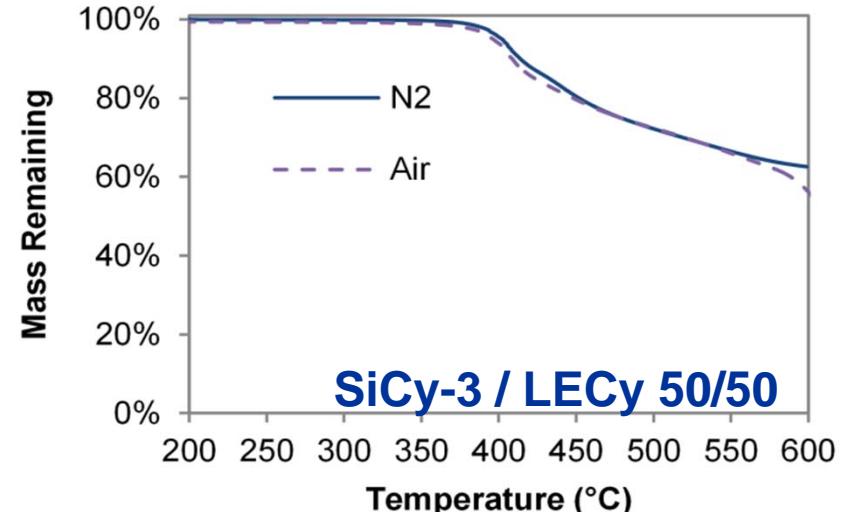
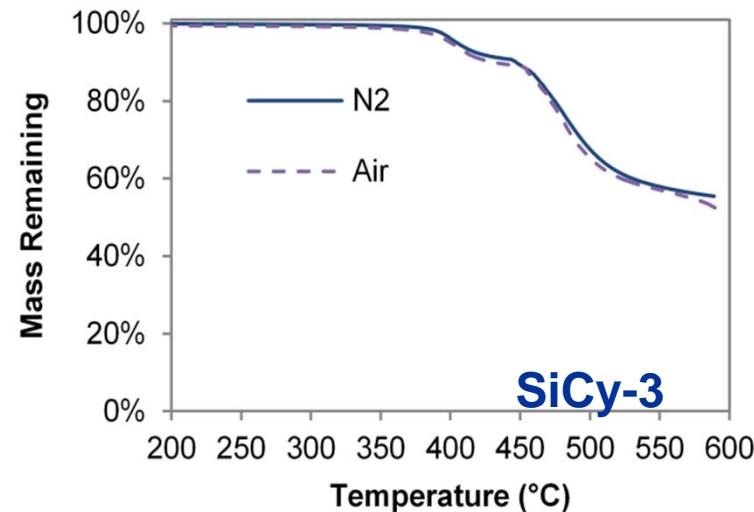
General Synthesis for Si-Containing Monomers



- SiMCy is the $n=2$ case (Si in network segment), $n=3$ or $n=4$ produces Si at network junctions.



Si-Containing Cyanate Esters: TGA Data





Si-Containing Cyanate Esters: Non-isothermal DSC



Comparative TGA Data for Cyanate Ester Monomers Cured at 210 °C for 24 hours

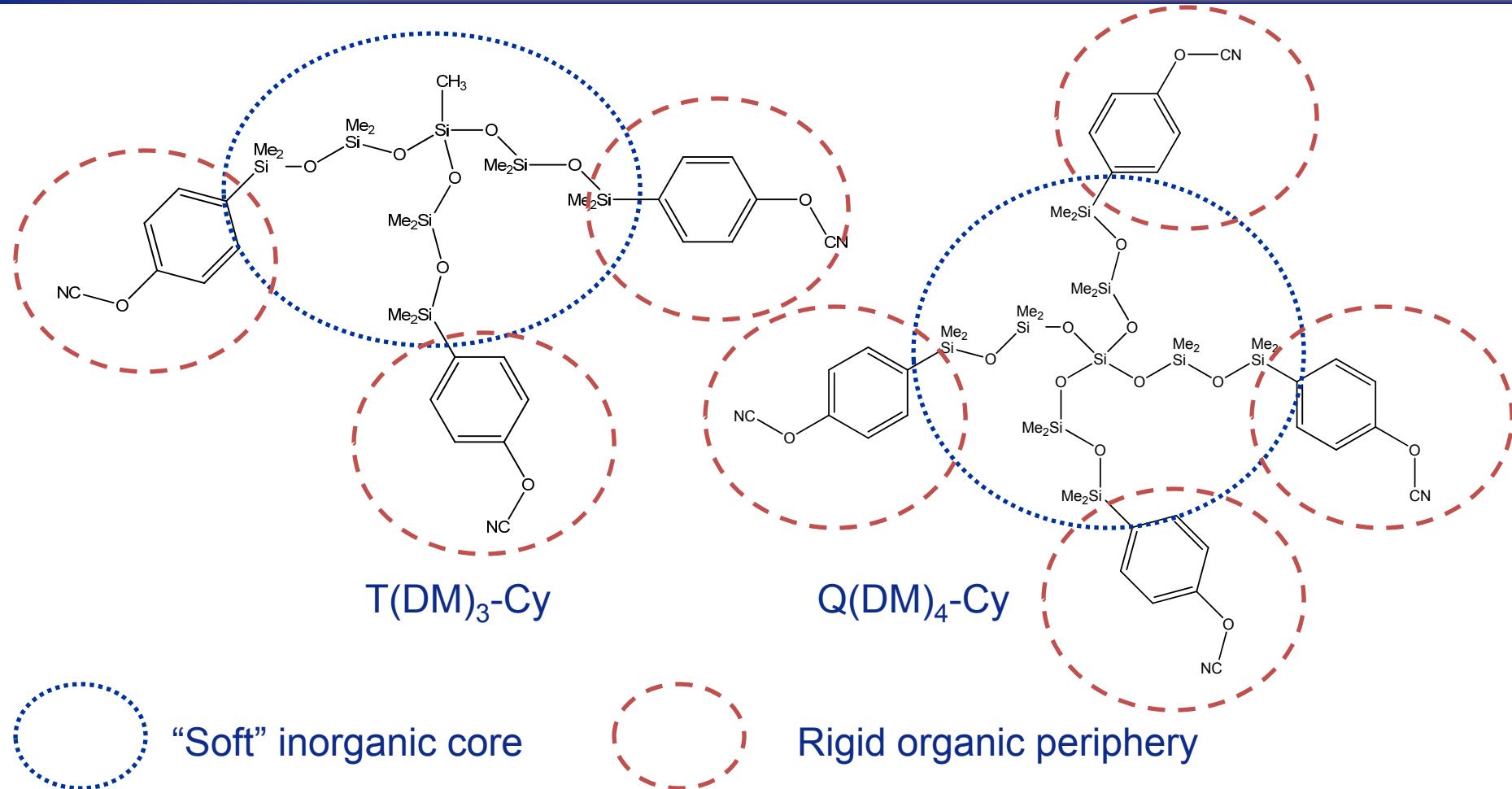
Monomer	Central Atom	<i>f</i>	Purification	T, 5% wt. Loss (in N ₂ , °C)	T, 5% wt. Loss (in air, °C)	Char Yield (in N ₂ , 600 °C)	Char Yield (in air, 600 °C)
BADCy	C	2	As-Rec'd	402	400	47%	25%
ESR-255	C	3	As-Rec'd	417	412	67%	59%
SiMCy	Si	2	As-Synth.	422 ^a	409 ^a	43%	50%
SiCy-3	Si	3	As-Synth.	405	400	55%	50%
SiCy-3 / LECy	Si	3 / 2	As-Synth.	402	396	63%	56%
SiCy-4 / LECy	Si	4 / 2	As-Synth.	409	395	70%	53%
ESR-255 / LECy	C	3 / 2	As-Rec'd	405	406	60%	2%

^a Estimated

- Substitution of Si for C at the bridge only improves char yields when those yields are low. For organic cyanate esters with high char yields, substitution of Si is not helpful.
- Incorporating monomers with greater functionality is most effective at raising char yields in nitrogen.



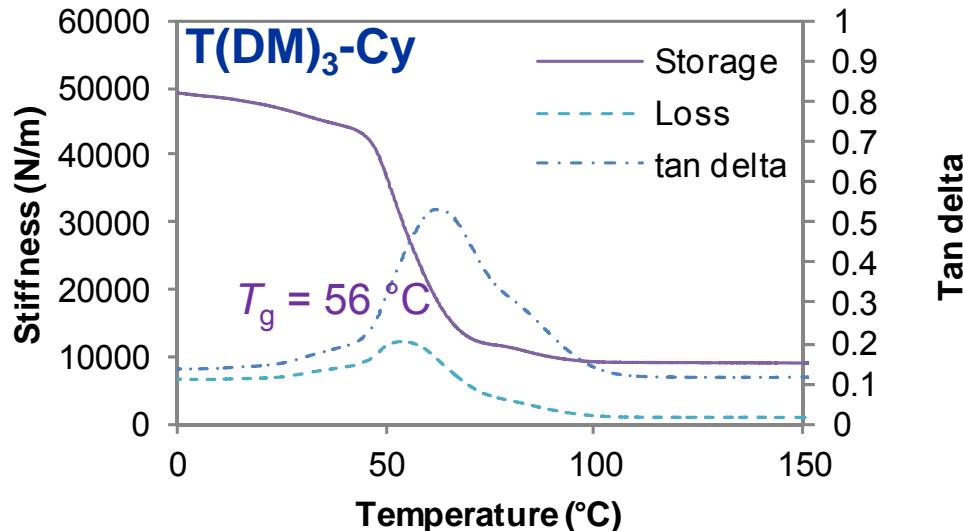
Siloxane-Containing Cyanate Esters



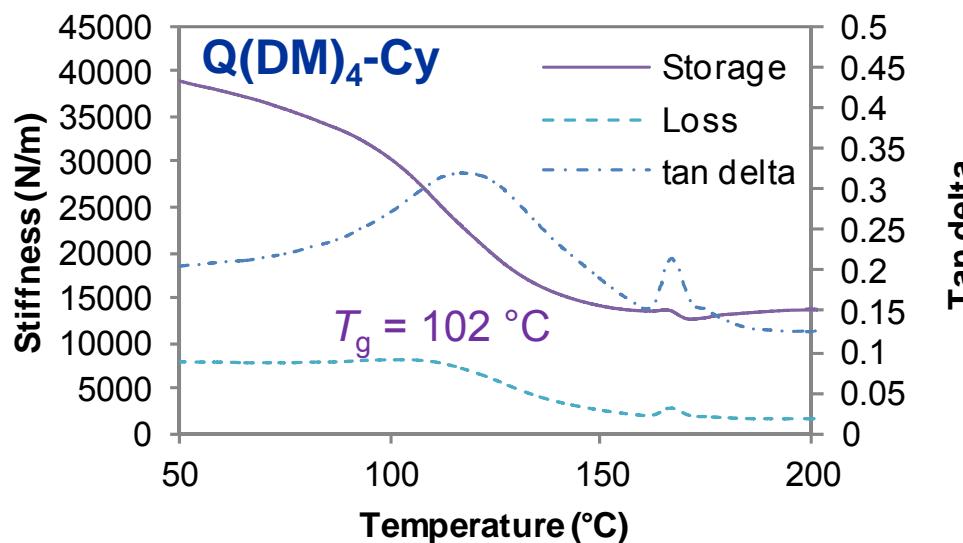
- Higher inorganic content expected to result in better char yields at temperatures over 600 °C.



Siloxy-Containing Cyanate Esters: Glass Transition Temperature

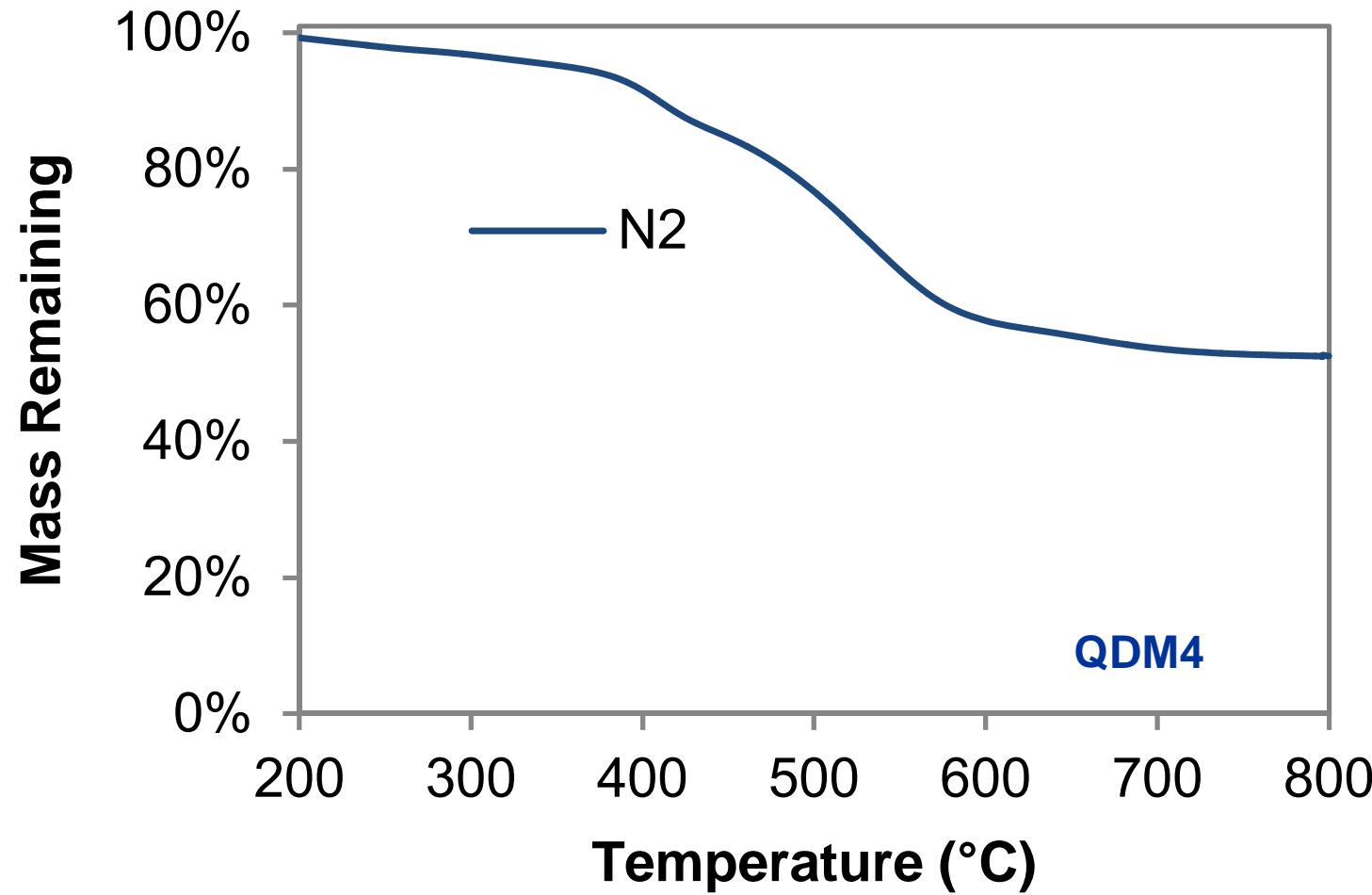


- Both cyanate esters showed a relatively low glass transition temperature for cyanate esters.
- The cyanurate density for these resins is roughly half that of typical cyanate esters.
- The branch point adds some stiffness, but not enough to make up for the long distance between network junctions.
- Further optimization of the cross-link and junction density will be needed to produce cyanate esters with both flexible core regions and high glass transition temperatures.





Siloxane Cyanate Esters: Preliminary TGA Data

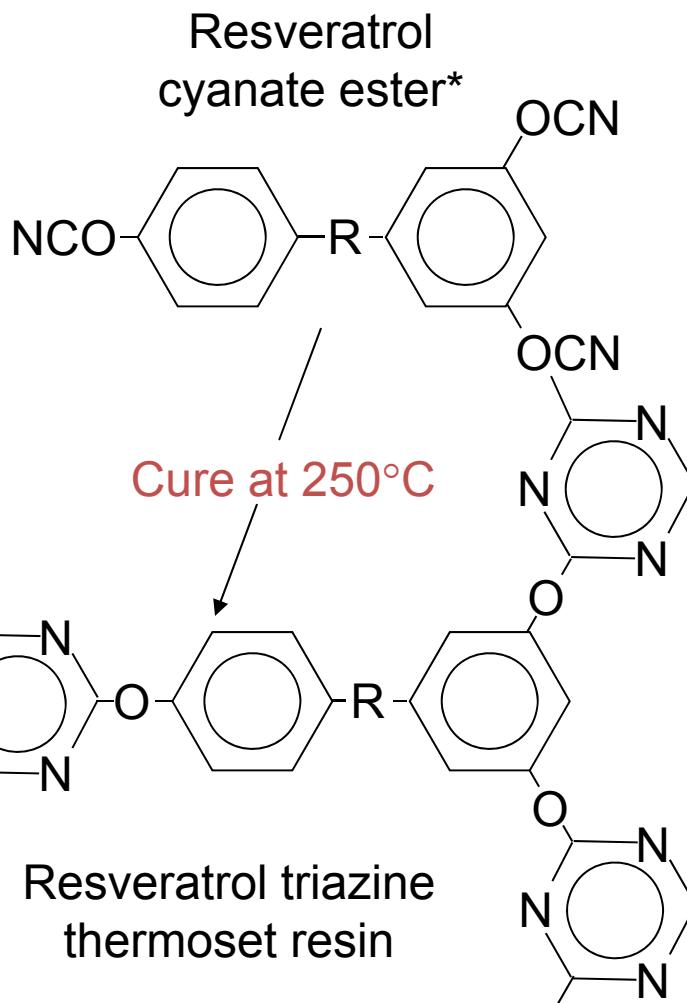
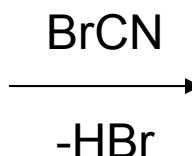
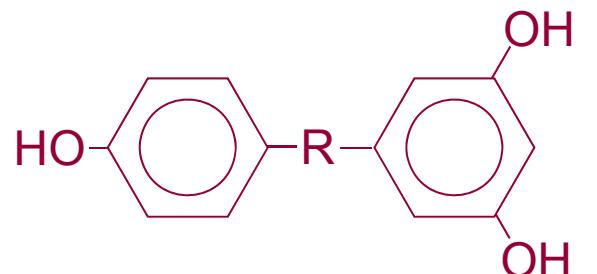




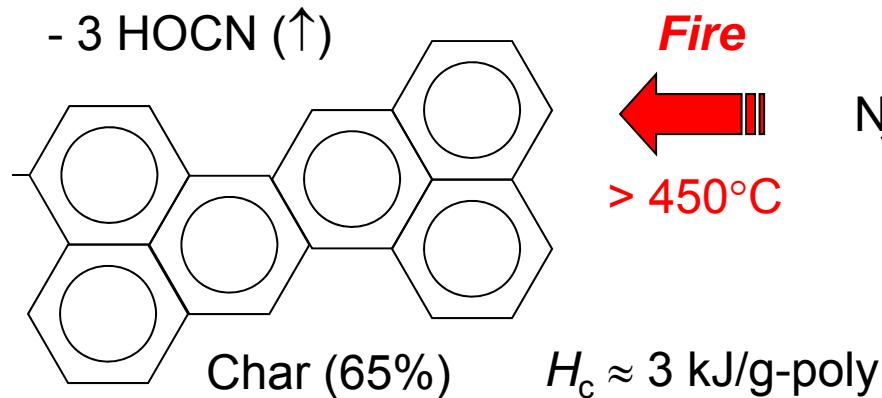
Fire-Resistant Cyanate Esters From Resveratrol



- Polyphenolic antioxidant used as a dietary supplement
 - Extracted from seaweed, red grapes, red wine



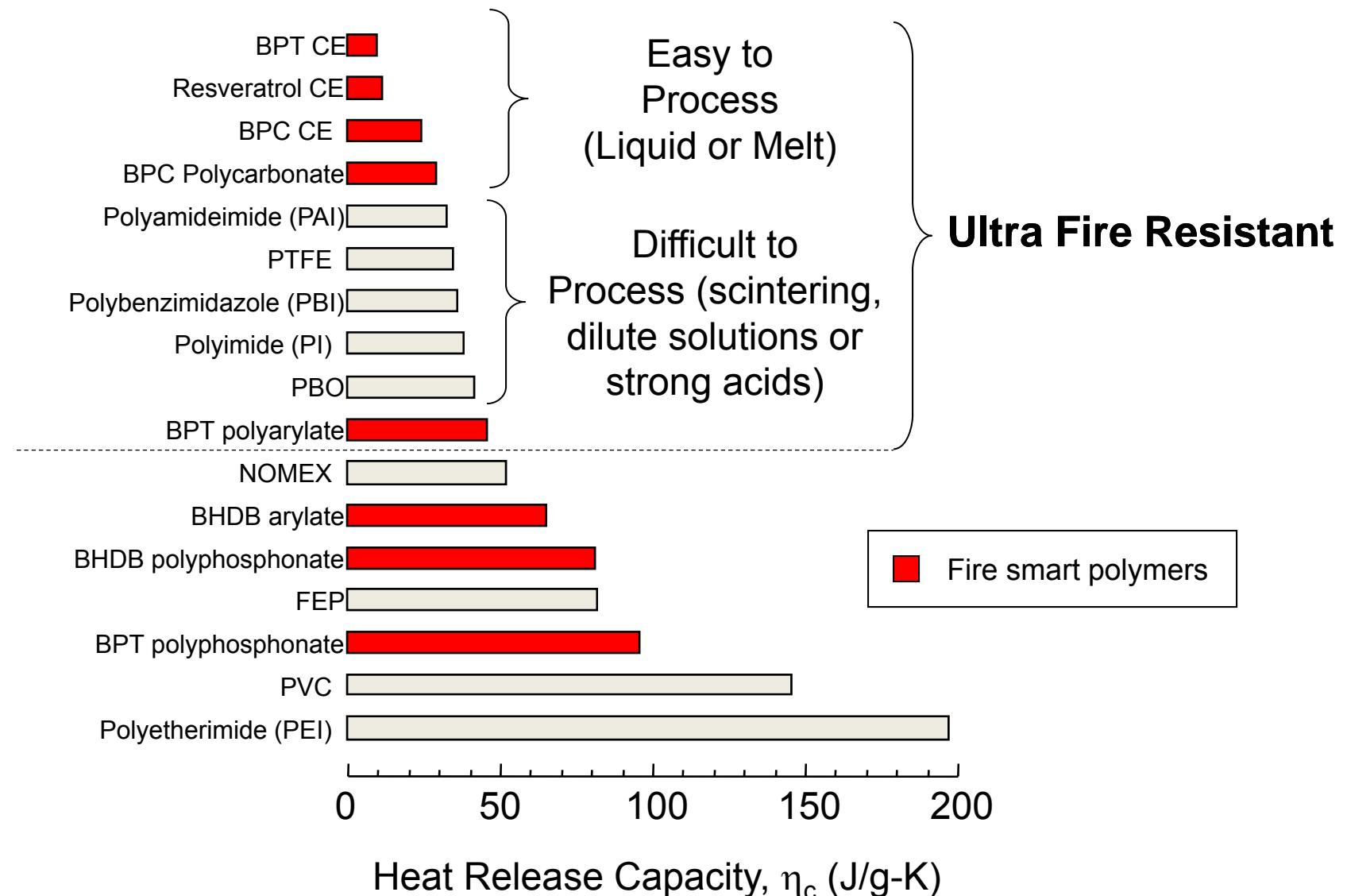
$R = -HC=CH-$, $= -CH_2-CH_2-$
(resveratrol) (dihydro resveratrol)



*B.J. Harvey, et. al., SERDP WP-2214 SEED Final Report, U.S. Navy, NAWCWD, China Lake, CA (2011), as presented by R. Lyons at Meeting High Performance Flammability Requirements for Aviation, Seattle, WA , April 2-3, 2014



Fire Smart Versus Current 65/65 Polymers



As presented by R. Lyons at Meeting High Performance Flammability Requirements for Aviation, Seattle, WA , April 2-3, 2014

DISTRIBUTION A: Approved for public release; distribution is unlimited.



Summary

- The short-term chemical stability of cyanurate networks appears to be optimal when segments and junctions containing tertiary or quaternary carbons are avoided (based on empirical observation but supported by studies in polycarbonate).
- Using combinations of methylene and phenylene junctions and spacers in cyanurate networks, the T_G -conversion characteristics can be tuned to match processing constraints without sacrificing thermochemical stability.
- Incorporation of inorganic Si or siloxane moieties in cyanate esters is only helpful for thermo-chemical stability at very high temperatures and when a large portion of the monomer consists of inorganic moieties.
- Cyanate esters based on resveratrol show good short-term thermo-oxidation resistance as well as very promising fire resistance characteristics based on preliminary investigations to date.

